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THE PINACOL-PINACOLONE MOLECULAR REARRANGEMENT

I. THE REARRANGEMENT OF PINACOL AND OF TETRAMETHYLETHYLENE CHLOROHYDRIN

II. THE REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL

A PART OF A DISSERTATION SUBMITTED TO THE FACULTY OF THE DIVISION OF THE PHYSICAL SCIENCES IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1932

By
KENNETH HOWARD ADAMS

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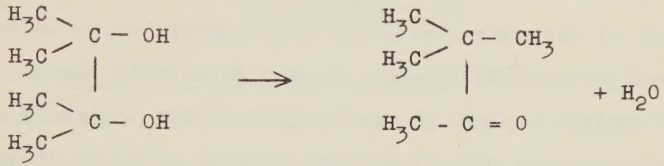
THEORETICAL PART

The pinacol-pinacolone molecular rearrangement which is represented by the following equation



has been the subject of numerous investigations since the discovery of the reaction by Fittig[1] in 1859. Of the numerous theories[2] which have been devised in attempts to discover the mechanism of the reaction none have been completely successful.

During the past few years Stieglitz has been developing an electronic interpretation[3] of the pinacol rearrangement which is an outgrowth of a similar theory which he has applied[4] to a large group of other rearrangements including Hofmann's rearrangement of acyl halogen-amines,[5] the Lossen rearrangement of

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[1]Fittig, Ann., 110, 25 (1859); 114, 54 (1860).

[2]See C. W. Porter, "Molecular Rearrangements" (New York: Chemical Catalog Co., 1928), pp. 85 ff.

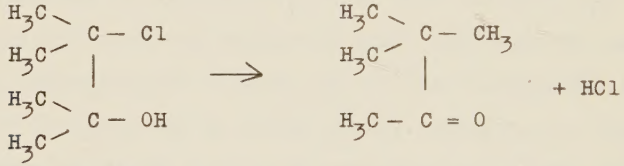
[3]Theory of J. Stieglitz reported in the Doctorate Dissertation of R. B. Cooper, University of Chicago, 1930; see Abstracts of Theses, The University of Chicago, Science Series, VIII (1929-30), 77. The experimental work of Cooper was started in January, 1927.

[4]The application of the electron theory of valence to the interpretation of molecular rearrangements was made independently and practically simultaneously by J. Stieglitz (J. Am. Chem. Soc., 36, 287 [1914]) and L. W. Jones (Am. Chem. J., 50, 448 [1913]).

[5]Stieglitz and Vosburgh, Proc. Nat. Acad. Sci., 1, 202 (1915).

hydroxamic acids,[1] the Curtius rearrangement of acyl azides,[2] and the rearrangements of certain triphenyl methane derivatives.[3]

Cooper,[4] as one of Stieglitz' collaborators, has investigated the effect of acids upon the rate of rearrangement of pinacol. In the present investigation some of this work has been repeated and confirmed with the aid of a different analytical method. Also the rearrangements of pinacol in neutral aqueous solution and of tetramethylethylene chlorohydrin in non-aqueous solution have been investigated. It was found that pinacol, which rearranges readily at 100° in acid solution, can be caused to undergo rearrangement also in neutral aqueous solution at temperatures near 200°. Tetramethylethylene chlorohydrin likewise was found to rearrange at 125° in benzene solution according to the following equation:



This is in agreement with the results of Ayers[5] who investigated tetramethylethylene bromohydrin. Finally, the rearrangement of another derivative of pinacol, β-aminotetramethyl ethanol, was studied. This compound, as was first reported by Krassusky,[6]

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[1]Stieglitz and Stagner, Proc. Nat. Acad. Sci., 1, 205 (1915); J. Am. Chem. Soc., 38, 2046 (1916).

[2]Curtius, J. Prakt, Chem., 95, 327 (1917).

[3]Stieglitz and Leech, J. Am. Chem. Soc., 36, 272 (1916).

[4]Cooper, Doctorate Dissertation, The University of Chicago, 1930; see Abstracts of Theses, The University of Chicago, Science Series, VIII (1929-30), 77.

[5]George W. Ayers, Doctorate Dissertation, The University of Chicago (1931).

[6]Ukrain Krassusky, Chem. J., 4, 61 (1929); Chem. Centr., 1929, 4, 2174.

rearranges in the presence of acids with the formation of pinacolone and an ammonium salt. It was desired to determine the effect of acids upon the rate of this reaction. The experimental methods and results of these investigations are included in this report.

EXPERIMENTAL PART

Preparation of anhydrous pinacol.--Pinacol hydrate was prepared by the reduction of acetone by means of magnesium and mercuric chloride in benzene solution.[1] The hexahydrate of pinacol thus obtained was purified by recrystallization from water and then dehydrated by distillation under reduced pressure. The practically anhydrous product was then redistilled from a Claisen flask under atmospheric pressure. The middle fraction, boiling range 171°-173°,[2] was sufficiently pure for most purposes. The redistilled product melted at 37°-38°.

Quantitative estimation of pinacolone.--In the course of his investigation of the rate of rearrangement of pinacol, Cooper devised a method for the estimation of pinacolone which was based upon an observation of Gillett[3] that this ketone forms a precipitate with Nessler's solution. For the purposes of the present investigation, especially that portion of it dealing with the rearrangement of the amino derivative of pinacol, Cooper's method was found to be not entirely satisfactory. Consequently, a new

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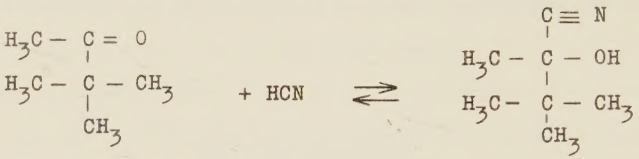
[1] Organic Syntheses (New York: John Wiley and Sons, 1925), Vol. V, p. 87.

[2] All thermometer readings recorded in this report have been corrected for exposed stem by the United States Bureau of Standards formula.

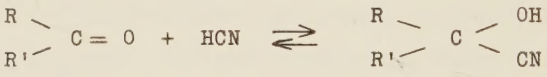
[3] Gillett, Bull. soc. chim., [4], 33, 465 (1923).

method for the estimation of the ketone was devised which was based upon the equilibrium reaction between pinacolone, hydrogen cyanide, and the cyanohydrin of pinacolone:



This type of reaction has been investigated quantitatively for numerous other ketones by several workers including Ultee,[1] Jones,[2] and Lapworth.[3] The results of these investigations show that the reaction between hydrocyanic acid and aldehydes or ketones displays the following characteristics:

1. In dilute solutions equilibria of the type



are established.

2. In the absence of cyanide ions the rate of reaction is very slow.

3. In alcohol solution the formation of the cyanohydrin is favored; water tends to dissociate the addition compound.

4. The equilibrium may be "frozen" by the addition of acids. The addition product is not stable in alkaline solution.

5. The cyanohydrin is progressively dissociated into its components with rise in temperature.

The results of our investigation of the equilibrium between pinacolone and hydrogen cyanide are in agreement, in so

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[1]Ultee, Rec. trav. chim., 28, 247 (1909); Ber., 39, 1857 (1906).

[2]Jones, J. Chem. Soc., 96, 1560 (1914).

[3]Lapworth, J. Chem. Soc., 85, 995 (1903); 130, 2052 (1927); 131, 2533 (1928); 133, 1976 (1930).

far as the general characteristics of the reaction are concerned, with those listed above. The equilibrium constant was measured at 0° in a mixed alcohol-water solution of composition comparable to that which would be used ultimately in the measurement of the rate of rearrangement of pinacol in aqueous solution.

The pinacolone used in the investigation was obtained from the Eastman Kodak Company. It was refractionated and that portion which boiled at $106^{\circ} \pm 0.1^{\circ}$ was used in the preparation of standard solutions of the ketone. Special precautions were observed to prevent loss of the volatile ketone during the process of weighing and transferring to the volumetric flask. Distilled water was used as the solvent.

Hydrogen cyanide was prepared by the reaction between sodium cyanide and sulphuric acid. A 20% solution of the former and a 35% solution of the latter were dropped simultaneously into a small mixing funnel suspended in the neck of a two-liter flask. The gaseous hydrogen cyanide passed through a calcium chloride drying tube and then condensed into a spiral condenser submerged in an ice-salt mixture. The liquefied hydrocyanic acid was collected in a small volume of absolute ethyl alcohol. This concentrated solution was diluted with aldehyde-free alcohol in such proportions as to make the resulting solution approximately 0.15 molar in concentration. The solution prepared in this manner and stored in the dark in paraffin-sealed bottles showed practically no change in concentration in the course of several months.

For the determination of the equilibrium constant, the following procedure was adopted: Into a 50.0 ml. volumetric flask were introduced in the order named 15 ml. of aldehyde-free ethyl alcohol, a measured volume of the standard pinacolone solution, 10.0 ml. of the standard solution of hydrogen cyanide, 0.5 ml. of

absolute alcohol saturated with potassium cyanide, and distilled water to make the total volume 50.0 ml. The flasks were closed with glass stoppers, sealed with paraffin, and suspended in an ice bath. After about one hour the volume of liquid in each flask was adjusted by the addition of alcohol, and the flasks were then left in the bath for 36 to 48 hours longer. The flasks were then opened one at a time and a 10.0 ml. sample removed from each with the aid of a pipette and aspirator. The sample was delivered into 10 ml. of a solution prepared by the addition of 44 g. of mercuric chloride and 23 g. of sodium chloride to one liter of water.[1] The liberated hydrochloric acid was titrated with a standard solution of sodium hydroxide with para-nitrophenol as the indicator. Since one mole of hydrochloric acid is produced for each mole of hydrocyanic acid present, the concentration of the latter in the equilibrium mixture may be calculated directly. The initial concentration of hydrocyanic acid was determined by analysis of the control sample which contained no pinacolone. The data for one set of determinations of the equilibrium constant are given in Table I.

TABLE I

EQUILIBRIUM CONSTANT FOR THE REACTION BETWEEN PINACOLONE AND HYDROGEN CYANIDE

Standard Solution of Pinacolone		1.0318 g./100 ml.
Vol. of Ketone Soln.	Vol. NaOH 0.04862 N.	$K_{eq} \times 10^3$
3.00	8.73	9.96
4.00	8.28	10.16
5.00	7.82	9.71
6.00	7.38	9.70
7.00	6.98	9.81
8.00	6.58	9.73
9.00	6.20	9.77
Control	10.19	

[1] Andrews, Am. Chem. J., 30, 187 (1903).

A solution of pinacolone of unknown concentration may be analyzed by the addition of a known amount of hydrocyanic acid under conditions identical with those employed in the determination of the equilibrium constant. After equilibrium has been attained the solution is analyzed for uncombined hydrocyanic acid. The difference between the initial and final concentration of hydrocyanic acid represents the concentration of the cyanohydrin. The total initial concentration of pinacolone is then equal to the sum of the concentrations of the cyanohydrin and the uncombined ketone, which is calculated with the aid of the equation

$$[\text{Ketone}] = \frac{[\text{Cyanohydrin}]}{[\text{HCN}]} \times K_{eq}.$$

Rate of rearrangement of pinacol in acid solution.--Approximately 1.2 g. of anhydrous pinacol was carefully weighed and transferred to a volumetric flask of 100 ml. capacity. The flask was filled to the mark with acid of the desired concentration, and about 11 ml. of the thoroughly mixed solution sealed in each of nine reaction tubes. The tubes were then simultaneously immersed in a bath of boiling water. The first sample was removed after about 4 minutes, and the other samples one by one after properly spaced intervals of time. After removal from the boiling water the tubes were plunged into ice water to stop the reaction, opened, and a 10.0 ml. sample transferred from each to a 50.0 ml. volumetric flask. The acid was neutralized by the addition of sodium hydroxide solution of sufficiently high concentration to keep the total volume of aqueous solution within 15 ml. Paranitrophenol was used as the indicator. To this carefully neutralized solution were added alcohol, hydrocyanic acid, and potassium cyanide in the proportions indicated above. In all respects the solutions were handled in a manner identical with that described in connection with the determination of the equilibrium constant.

A typical set of data for the determination of the rate of rearrangement of pinacol in 0.54 molar hydrochloric acid is given in Table II. In this table, A represents the weight of anhydrous pinacol which was dissolved in B ml. of acid; C represents the volume of the sample of the reaction mixture which was used in the pinacolone analysis. The time of removal of the sample is given in the first column, the volume of sodium hydroxide solution required to neutralize the uncombined hydrocyanic acid is given in the second column, the calculated concentration of pinacol in the third column, and the monomolecular reaction rate constant in the last column.

TABLE II

REARRANGEMENT OF PINACOL IN 0.54 M. HCl AT 100° C.

A = 2.2514 g. B = 200 ml. C = 10.0 ml.

Time in Minutes	Vol. NaOH 0.03088 N.	Conc. of Pinacolone	$K_v \times 10^2$
0	9.50	0.01006	
8	8.80	0.02491	2.39
18	8.10	0.04051	2.45
28	7.58	0.05260	2.47
40	7.11	0.06408	2.51
55	6.75	0.07327	2.46
75.2	6.39	0.08289	2.55
106	6.15	0.08955	2.41
Control	9.99	Average	2.46
		Cooper's value	2.49

In 1.08 molar hydrochloric acid solution the average value of $K_v \times 10^2$ was found to be 5.58, which is in good agreement with Cooper's value of 5.48.

Rearrangement of pinacol in neutral aqueous solution.--The pinacol hydrate which was used in these experiments was prepared by the hydration of pure anhydrous pinacol. Recrystallization of the hydrate from distilled water yielded a product which was completely odorless and melted sharply at 46.0° - 46.5°. A

solution of 15 g. of pinacol hydrate in 20 ml. of conductivity water was sealed in a "pyrex" glass bomb tube in an atmosphere of nitrogen. After the tube had been heated at 210° for 10 hours a layer of about 5 ml. of a liquid with the odor of pinacolone had collected upon the surface of the aqueous solution. Most of the lighter liquid boiled within the range of 103°-108°, although approximately 0.7 g. of a viscous, non-volatile residue remained in the distilling flask. The 103°-108° fraction was identified as pinaculone by the formation of the semicarbazone which melted at 156°. From the aqueous solution was recovered 3 g. of unchanged pinacol hydrate.

Preparation of tetramethylethylene chlorohydrin.--Pure anhydrous pinacol (50 g.) was placed in a small round-bottom flask which was equipped with a stirring device. A stream of dry hydrogen chloride was passed into the melted pinacol at a temperature of 40° ± 5° for a period of 6 to 8 hours, or until a small sample of the reaction mixture solidified in ice water with the formation of a wax-like globule which was free from the characteristic flaky crystals of pinacol hydrate. The amber liquid was then poured into ten volumes of cold water and the mixture stirred rapidly. The tetramethylethylene chlorohydrin separated as a white solid which was collected upon a Buchner funnel and partially dried upon a porous plate. The yield of the crude product was 46 g. or 80% of the theoretical. The substance was purified by crystallization from 40°-50° ligroin. After being dried for an hour in a small desiccator over phosphorus pentoxide and paraffin the crystals melted at 62°-63°. Chlorine analyses were made by decomposition of the sample in two ways; first, by ignition in the presence of sodium peroxide and sugar in a Parr sulphur bomb, and second, by hydrolysis in the presence of sodium hydroxide in a sealed tube.

Analysis.--Parr bomb method: Substance: 0.1249 g.; AgCl: 0.1304 g.; Cl: found, 25.83%. Hydrolysis method: Substance: .0778 g.; AgCl: 0.0816 g.; Cl: found, 25.95%; calculated, 25.98%.

Pyrolysis of tetramethylethylene chlorohydrin.--A solution of 5 parts of pure chlorohydrin in 100 parts of dry benzene was left in contact with anhydrous sodium sulphate for 24 hours. Small portions of this solution were sealed in "pyrex" glass bomb tubes; care was taken to prevent the entrance of moisture during the sealing off process. Two of these tubes were heated for six hours at 100°, two were heated for four hours at 125°, and two were placed in an oil bath at 175°. One of the latter was removed after 30 minutes and the other one after one hour. One-half of the contents of each tube was tested for the presence of pinacolone by the addition of an equal volume of Nessler's solution. The remainder of each solution was washed with cold alcohol into 5 ml. of ice-cold water and the free hydrogen chloride immediately estimated by titration with a solution of sodium hydroxide and p-nitrophenol. The aqueous solutions were allowed to stand at room temperature for 6 hours in order to hydrolyze the undecomposed tetramethylethylene chlorohydrin. In this manner it was possible to estimate roughly the fraction of the chlorohydrin which decomposed during the heat treatment.

The samples which were heated at 100° yielded no precipitate with Nessler's solution, and were found to contain no free hydrogen chloride. The solutions which were heated at 125° yielded a small precipitate with Nessler's solution; by titration it was found that only a small fraction (less than 5%) of the tetramethylethylene chlorohydrin had undergone rearrangement. The sample which was heated for 30 minutes at 175° required 1.4 ml. of .033 N. hydrochloric acid for the initial titration, and 4.2 ml.

for the final titration. These results indicate that approximately 25% of the chlorohydrin had decomposed. The sample which was heated for an hour at 175° showed 50% decomposition. Both solutions yielded precipitates with Nessler's solution.

Preparation of β-aminotetramethyl ethanol.--This compound was prepared by a modification of the method used by Krassusky.[1] Crude tetramethylethylene chlorohydrin (40 g.), prepared as described above (p. 9) was sealed in a steel bomb tube with 250 ml. of ammonium hydroxide solution which had been previously saturated with ammonia at -5°. The mixture was allowed to stand at room temperature for two hours and was then heated in a steam bath at 100° for 60 hours. The bomb tube was cooled in an ice-salt mixture and opened. The contents, which has become homogeneous, were mixed with cracked ice and made neutral by the addition of concentrated hydrochloric acid. The precipitated ammonium chloride was removed by filtration and the filtrate evaporated to dryness over a water bath. The residue was heated for three hours at 110°, after which it was extracted with three portions of 75 ml. each of absolute ethyl alcohol. The combined extracts were evaporated to dryness and the residue again extracted with 50 ml. of absolute alcohol. A residue of 3 g. of ammonium chloride remained. From the alcohol solution a bulky precipitate of β-aminotetramethyl ethanol hydrochloride was obtained upon the addition of three volumes of dry ether. The yield of the crude product was 26 g. The free amino alcohol was obtained by addition of the hydrochloride to 15 ml. of a saturated solution of potassium hydroxide and an excess of the powdered alkali. The amino alcohol separated as a light yellow oil which was completely

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[1] Loc. cit.

removed from the aqueous solution by extraction with ether. The ether extract was dried with solid potassium hydroxide and then subjected to fractional distillation. The middle fraction, which had a boiling point of 163°-164° under a pressure of 753 mm., was collected and redistilled under reduced pressure. The boiling point was 42° at 8 mm. The yield was 11 g. or 30% of the theoretical. The product was analyzed by titration with standard acid and methyl red: 0.1423 g. and 0.2403 g. required 28.36 ml. and 47.94 ml. of 0.04272 N. HCl. Calculated for C_6H_5ON, 28.44 ml. and 48.02 ml.

Preparation of β-aminotetramethyl ethanol hydrochloride.--The free amino alcohol, prepared and purified as described, was dissolved in dry ether and a slow stream of dry hydrogen chloride was passed into the solution. The white precipitate of β-aminotetramethyl ethanol hydrochloride was collected upon a funnel, washed with dry ether, placed in a desiccator over solid potassium hydroxide for two hours, and then heated in a vacuum at 110° to remove traces of ether and water. The product melted sharply at 218°. Analysis for ionizable chlorine yielded the following results: Subst.: 0.3078 g., 0.1970 g. AgCl: 0.2873 g., 0.1840 g. Calcd. for C_6H_6ONCl, 23.08% Cl. Found 23.09% and 23.11%.

The thermostat.--The thermostat was constructed from a piece of steel tubing 10 inches in diameter and 12 inches long. Over one end was brazed a piece of sheet steel one-eighth of an inch thick. The capacity of the vessel was about 4 gallons. The walls were insulated with corrugated asbestos pipe covering. The vessel was filled with a heavy grade of motor oil, which was heated by an electric hot plate to a temperature about 10° below that used in the experiments. The final control of the temperature was provided by a 100 watt electric light bulb which was operated in the usual manner by a relay and mercury-in-glass

thermo-regulator. The oil was kept in constant motion by means of a motor-driven stirrer. It was possible to control the temperature to within 0.1° of the desired point, which was 175° in most of the experiments. A calibrated thermometer, graduated in tenths of a degree was used.

Analytical methods.--The determination of the rate of rearrangement of β-aminotetramethyl ethanol was based upon the analyses of the reaction mixtures for unchanged amino alcohol; some of the reaction mixtures were analyzed also for pinacolone. The former of these analyses were conducted according to a modification of the method of Erdmann[1] for the determination of aliphatic amines in the presence of ammonia. A 10 ml. sample of the solution containing ammonia, unchanged amino alcohol, and pinacolone was diluted to 35 ml. with distilled water and made slightly acid with hydrochloric acid. The solution was boiled for about four minutes to remove pinacolone and after it had become cool it was made alkaline by the addition of 10 ml. of a 10% solution of potassium hydroxide. A saturated solution of mercuric chloride was slowly added to the mixture which was shaken constantly until the white precipitate of mercuric amino chloride contained an excess of yellow mercuric oxide. The flask was tightly stoppered and placed in a dark cupboard for at least 24 hours. The contents of the flask were frequently agitated in order to keep part of the mercuric oxide in suspension. On the following day the precipitate was removed by filtration. After the addition to the filtrate of 40 ml. of a 50% solution of sodium hydroxide the amine was distilled into a measured volume of standard acid and the excess acid then titrated with sodium hydroxide solution; methyl red was used as the indicator. The distillate

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[1]Erdmann, J. Biol. Chem., 8, 41 (1910).

was found invariably to contain traces of ammonia as indicated by the Nessler test. Suitable correction for this was made by Nesslerization of the distillate. Color standards were prepared from a solution of ammonium chloride in accordance with the directions of "Standard Methods of Water and Sewage Analysis."[1] In order to correct for the color produced by the presence of methyl red in the distillate to be Nesslerized, an equal amount of the indicator was added to the water used in the preparation of the color standards.

The quantitative method for the estimation of pinacolone, which has already been described, was found to be adaptable, with slight modifications, to the present investigation of the rearrangement of β-aminotetramethyl ethanol. Methyl red was used as the indicator in place of p-nitrophenol. All of the samples of one run were analyzed simultaneously, and at the same time a determination of the constant for the equilibrium between pinacolone and hydrogen cyanide was also made.

Rearrangement of β-aminotetramethyl ethanol hydrochloride.--A solution of 2.0 g. of the pure salt dissolved in 4 ml. of distilled water was sealed in a bomb tube in an atmosphere of nitrogen and heated for 8 hours at 210°-215°. At the end of that period 1.5 ml. of liquid with the odor of pinacolone had collected upon the surface of the aqueous solution. The liquid was separated from the latter and added to 10 ml. of water which contained 2 g. of semicarbazide hydrochloride and 2 g. of sodium acetate. The characteristic bulky precipitate of pinacolone semicarbazone formed readily, which melted, after recrystallization from light petroleum ether, at 158°. The yield of the crude semicarbazone was 1.9 g., which corresponds to 1.9 g. of

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[1] Am. Public Health Association, New York (1925).

β-aminotetramethyl ethanol hydrochloride. The aqueous solution which remained after separation of the pinacolone was distilled. The first portion of the distillate (about 2 ml.) was tested for the presence of acetone by the benzylidene acetone test. The presence of acetone was not indicated. The residue in the distilling flask was evaporated to dryness and washed with absolute alcohol. White crystals of ammonium chloride (0.7 g.) remained. The alcohol extract upon evaporation yielded no residue other than a trace of ammonium chloride and a very small amount of gum.

The quantitative study of the rate of rearrangement of β-aminotetramethyl ethanol hydrochloride was conducted in the following manner. Approximately 1.55 g. of the pure salt was accurately weighed into a volumetric flask of 100 ml. capacity. Freshly boiled distilled water was used as the solvent. A sample of the solution, approximately 11 ml. in volume, was transferred to each of nine reaction tubes made of "pyrex" glass. The tubes were sealed, placed in wire gauze protectors, and immersed in a beaker of oil, the temperature of which was 90°-100°. After about five minutes the samples were transferred simultaneously to the 175° constant temperature bath. Within 30 minutes the first sample was removed, and the time noted. The sample was cooled first to 100° and then to room temperature. At properly spaced intervals of time the other samples were removed. A 10 ml. sample from each tube was analyzed for unchanged amino alcohol according to the method described above.

Table III gives the details of the experimental data for a typical determination. A represents the weight of the sample of β-aminotetramethyl ethanol hydrochloride, and B the volume of the solution of that compound from which the reaction tubes were filled. Column 1 gives the time of removal of the samples; column

TABLE III

REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL HYDROCHLORIDE, 0.1 M. AT 185°

A = 3.0471 g.		B = 200 ml.		C = 250 ml.	
Time Hours	Vol. HCl .04271 N.	Vol. NaOH .03334 N.	Nessler Test MgN 50 ml.	Net Conc. Amine	$K_v \times 10^3 \times 4.342$
0	25.00	2.50	0.5	.09826	
6	25.00	7.05	0.5	.08309	121.4
12	25.00	10.80	1.0	.07044	120.5
25.08	20.00	10.90	0.4	.04882	120.6
47.08	20.00	17.40	1.1	.02702	121.2
59	15.00	13.20	2.0	.01933	119.6
71	15.00	14.73	1.1	.01456	116.9
83	10.00	9.34	1.2	.01114	114.0

TABLE IV

REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL HYDROCHLORIDE 0.1 M. AT 185°

Pinacolone Analysis

Time Hours	Vol. NaOH .03334 N.	Conc. of Pinacolone	Calculated Conc. of Pinacolone
6	7.61	.01631	.01666
12	7.07	.02839	.02931
25.08	6.22	.04845	.05093
47.08	5.30	.07232	.07273
59	5.00	.08078	.08042
71	4.80	.08667	.08519
83	4.76	.08786	.08861
102	4.59	.09308	(.09064)
Control	8.37		

Equilibrium Constant

Standard solution of Pinacolone		0.6920 g. 100 ml.
Vol. of Ketone Soln.	Vol. NaOH .02752 N.	$K_{eq} \times 10^3$
4.00	9.49	7.70
6.00	8.74	7.45
7.00	8.35	7.01
8.00	8.02	7.30
9.00	7.70	7.49
10.00	7.33	7.11
12.00	6.76	7.61
14.00	6.15	7.41
15.00	5.82	7.10
Control	11.04	

2, the volume, in ml., of hydrochloric acid into which the amino alcohol was distilled; column 3, the volume of sodium hydroxide solution required to neutralize the excess of acid after distillation of the amine. Column 4 indicates the results of the Nesslerization of the distillate; the results are expressed in terms of milligrams of nitrogen in 50 ml. of the distillate, the total volume of which is indicated by the letter C at the head of the table. Column 5 expresses the net concentration of the amino alcohol present in the sample, while the last column gives the monomolecular reaction rate constant. The data for the analysis of the reaction mixtures for pinacolone by the hydrogen cyanide method are given in Table IV. Comparison of the concentration of the ketone as determined by this method with the theoretical concentration calculated upon the assumption that the amino alcohol was converted exclusively into pinacolone and ammonia (column 4 of Table IV), shows that the former was usually slightly lower than the latter.

Rearrangement of β-aminotetramethyl ethanol in alkaline and acid solution.--In addition to the measurements of the rate of rearrangement of β-aminotetramethyl ethanol hydrochloride in neutral aqueous solution, determinations of the reaction rates were also made for the rearrangement of the free base in 0.1 molar solutions to which varying amounts of hydrochloric acid were added. It was the intention to parallel as closely as possible the previous experiments on pinacol. Inasmuch as the amine alcohol is a fairly strong base ($K_I = 6.4 \times 10^{-5}$) practically all of the hydrochloric acid added to a solution of the free base combines with it to form a salt, and the reaction mixtures in those cases in which not sufficient hydrochloric acid is added to neutralize all of the amino alcohol consist of mixtures of

TABLE V

REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL
0.1 M. IN 0.025 M. HCl AT 175° C.

A = 2.4128 g.		B = 200 ml.
Time Hours	Conc. of Amine	$K_V \times 10^3$ x 4.342
0	.10295	
25.0	.09543	13.2
51.5	.08702	14.1
87.5	.07867	13.3
159.5	.06248	13.6
279.5	.04372	13.3
477.5	.02236	13.9

TABLE VI

REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL
0.1 M. IN 0.050 M. HCl AT 175° C.

A = 1.3114 g.		B = 100 ml.
Time Hours	Conc. of Amine	$K_V \times 10^3$ x 4.342
0	.11173	
12.00	.10581	19.7
26.00	.09895	20.3
47.50	.08837	21.4
84.50	.07531	20.2
127.75	.06174	20.5
203.00	.04423	19.8
299.00	.02954	19.4
413.00	.02065	17.7

TABLE VII

REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL
0.1 M. IN 0.075 M. HCl AT 175° C.

A = 1.2295 g.		B = 100 ml.
Time Hours	Conc. of Amine	$K_V \times 10^3$ x 4.342
0	.10474	
14.33	.09545	28.1
25.25	.08882	28.3
36.75	.07963	(32.3)
58.75	.07102	28.7
96.25	.05576	28.4
154.00	.03949	27.5
254.00	.02121	27.3

the alkamine hydrochloride and the free base. Results of the experiments are given in Tables V-VII. In these tables, A represents the weight of β-aminotetramethyl ethanol (free base), and B the volume of the solution of that compound from which the reaction tubes were filled. Analysis of the data has shown that the measured value of the reaction rate constant (K_v) is essentially the sum of the reaction rate constant for the rearrangement of the salt of the amino alcohol at the concentration corresponding to the amount of hydrochloric acid added to the reaction mixture plus a small effect probably due to the rearrangement or decomposition of the free base itself.

In the case of several of these experiments, the reaction mixtures were analyzed for pinacolone as well as for unchanged amino alcohol, but in every case the reaction rate constants were based upon the latter of these analyses. Typical results, as presented in Table VIII, show that the actual concentration of the ketone was always slightly lower than the theoretical concentration calculated upon the assumption that the amino alcohol was converted exclusively into pinacolone and ammonia. A qualitative examination indicated the presence in the reaction mixture of a small quantity of viscous, high-boiling material, the composition of which has not been determined.

Finally, it was desired to determine the effect of excess acid (more than that required for neutralization of the alkamine base) upon the rate of rearrangement of the amino alcohol hydrochloride. These measurements were made with solutions in which the initial concentration of β-aminotetramethyl ethanol hydrochloric acid ranged from 0.1 molar to 2.0 molar. A summary of the data is given in Table IX. It is evident that hydrochloric acid does accelerate the rearrangement of the alkamine

TABLE VIII

REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL
0.1 M. IN 0.05 M. HCl AT 185° C.

Pinacolone Analysis

Time Hours	Conc. Pinacolone Found	Conc. Pinacolone Calculated
4.00	.00623	.00760
12.05	.02045	.02221
23.12	.03295	.03569
27.50	.03677	.04156
44.00	.05136	.05713
69.00	.06402	.07370
112.00	.07518	.08626
161.50	.08376	.09417

hydrochloride, but the catalytic effect is not a linear function of the acid concentration. The theoretical aspects of these results are being further investigated.

TABLE IX

REARRANGEMENT OF β-AMINOTETRAMETHYL ETHANOL
HYDROCHLORIDE IN ACID SOLUTION

Conc. of HCl	$K_v \times 4.342 \times 10^3$	Temp.
0.00	35.5	175°
0.1011	108	175°
0.5115	251	175°
1.0398	312	175°
2.0796	356	175°
0.0	121	185°
0.1005	317	185°